THE SPECTRA OF SULPHUR DIOXIDE

A DISSERTATION

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BY

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I. THE ABSORPTION SPECTRUM

I. HISTORY

The absorption spectrum of sulphur dioxide was investigated in the ultraviolet region by W. A. Miller[1] in 1863. He inclosed the gas in a previously exhausted brass tube, two feet in length, the ends being closed by quartz plates. His source of radiation was the silver spark. He found that the silver spectrum was transmitted from scale-reading 96.5 to 110.5, at which point it was abruptly cut off. Estimated from a curve plotted from his maps, this range appears to be from λ 420 to 345 $\mu\mu$. He does not say at what pressure the gas was inclosed in the tube.

In 1883 Professors Liveing and Dewar[2] found that sulphur dioxide produced an absorption band "very marked between R (3179) and wave-length 2630, and a fainter absorption extending on the less refrangible side to O(3440), and on the other side to the end of the range photographed, wave-length 2300." They used as source of light the iron spark, and obtained the spectrum by means of a spectrometer having a single quartz prism and quartz lenses.

The present investigation was undertaken at the suggestion of Professor J. S. Ames, of Johns Hopkins University, and carried out at Bryn Mawr College.

II. APPARATUS AND METHOD

For the greater part of the work the gas was inclosed in a steel tube, 207 cm long, having its ends closed with quartz plates. It was provided with two pin valves for exhaustion of the tube and admission of the gas. The spectral apparatus was a quartz spectrograph of middle size by Fuess, used with a Rowland plane reflection grating having 14,438 lines to the inch.

[1] *Phil. Trans.*, 152, II, 861–887, 1863.

[2] *Proc.. R. S*, 35, 71–74, 1883.

In the region λ 690 to 390 $\mu\mu$ the carbon arc was used as source of light. In the region λ 410 to 210 $\mu\mu$ the source of light was the spark of an alloy of cadmium and zinc in proportions of their atomic weights. The beam was made parallel by a quartz lens before it entered the tube; on emergence it was brought, by another quartz lens, to a focus on the slit of the spectrograph. To obtain a continuous background with this spark, since no alternating current was available, the current from ten secondary cells was supplied to the primary of a ten-inch induction coil, and a capacity of 0.03 mfd. was placed across the terminals of the secondary, in parallel with the spark.

Before use the steel tube was thoroughly cleaned with hot potassium hydroxide and distilled water, and then thoroughly dried. The tube was exhausted by a water aspirator to about 1½ cm pressure, filled with sulphur dioxide to a pressure greater than one atmosphere, and again exhausted; after this process had been repeated several times, the tube was filled with sulphur dioxide to the desired pressure. The sulphur dioxide was obtained from liquid sulphur dioxide; the high temperature of liquefaction (—10° C.) of this gas insures its purity from other gases except air, which may be present in the gas above the liquid. Before using any of the gas a considerable quantity was allowed to escape to insure that the following supply of gas should be free from air. Before admission into the tube, the sulphur dioxide was passed through a tube containing phosphorus pentoxide to insure its dryness.

The photographic plates used were Seed's No. 27 Gilt Edge. An exposure of two hours was given for the absorption spectrum in every case. A comparison spectrum was photographed on the same plate as the absorption spectrum immediately above or below the latter.

Standard wave-lengths were obtained from the lines of *Cd*, *Zn*, *Pb*, and *Fe*, which were transmitted in sufficient numbers in the absorption spectrum, the *Pb* and *Fe* being present as impurities; by this means errors were avoided that might arise from disturbance of the apparatus in changing from the arrangement for the absorption spectrum to that for the comparison or another standard spectrum.

The absorption spectrum of sulphur dioxide in the violet and ultra-violet regions was found for pressures of three atmospheres, two atmospheres, and one atmosphere, 1½ cm, 0.45 cm, and 0.13 cm. The wave-lengths were determined by measurements made on the photographic plates in the usual way. The dividing engine used for this purpose was one by Gaertner, on which readings could be made to 0.0001 mm; that is, to a greater accuracy than settings could be made on the bands. The reduction factor was roughly 32 tenth-meters to 1 mm.

III. RESULTS

In the region λ 690 to 390 $\mu\mu$ no absorption bands are found. In the region λ 410 to 210 $\mu\mu$ the photographs show that the absorption spectrum, except at very low pressures of the gas, consists of one very wide band and a number of comparatively narrow bands of different widths and intensities. Tables I and II give the wave-lengths and intensities of the bands. The intensities are estimated by eye from the photographic plates; the scale is from 10 to ½, 10 being the maximum and applied to bands at whose center of gravity none of the continuous background is transmitted. In many cases it is difficult to obtain accurate values of the wave-lengths; in some cases this is due to the width of the band—e. g., 3, 8, or 11 tenth-meters, while in other cases it is due to the presence of a metal line which falls within the absorption band and is strong enough to be transmitted when the continuous background is absorbed. This limitation in accuracy is apparent on comparing the readings for the same line as given in parallel columns in the tables which follow.

A tube filled with oxygen at one atmosphere's pressure and sulphur dioxide at one atmosphere's pressure gave the same spectrum as the tube filled with sulphur dioxide only at one atmosphere's pressure.

In the tables, s. denotes sharp, b. broad, n. narrow, h. hazy, i.d. ill defined, and v. very.

TABLE I

ABSORPTION SPECTRUM OF SULPHUR DIOXIDE AT DIFFERENT ATMOSPHERIC PRESSURES

λ for 3 Atmos. Pressure	Intensity and Character	λ for 2 Atmos. Pressure	Intensity and Character	λ for 1 Atmos. Pressure	Intensity and Character
3881.7	9b.	3881.5	6	3881.8	1
3878.4	2s.	3878.7	3	3878.8	1n.
3828.3	10b.	3828.5	6	3828.5	2
		3825.3	3	3825.2	1n.
3776.3	3	3776.3	2	3776.4	½
3750.6	10b.	3751.1	8	3751.0	3b.
		3747.0	5s.	3747.0	2
3701.9	10v.b.	3701.7	10b.	3701.3	5s.
				3698.9	2n.
3657.4	2s.	3657.5	3n.	3657.6	1
3654.4	1	3654.4	3	3654.1	1
3650.6	1s.	3650.6	3n.	3650.7	1
3635.4	4b.	3635.4	4b.	3636.2	1b.
		3628.4	1		
		3623.5	2		
3593.9	4b.	3594.2	4v.b.	3594.2	1
3579.0	8b.	3579.1	5b.	3579.2	2
3532.8	9b.	3532.4	5b.	3532.5	1
		3529.6	3n.	3529.6	½
		3522.2	1		
		3512.3	½		
3509	f.b.	3510.1	1		
		3507.2	1		
3504	f.n.	3503.5	½		
3494.2	1	3494.1	1		
3490.1	1	3490.2	1		
3486.8	1	3486.2	½		
3474.7	1s.	3474.8	½		
3442.6	4b.	3443.2	4b.	3443.2	1
3434.1	1	3435.1	2		
3431.7	1	3432.2	2		
3423.9	2				
3422.6	3	3422.1	1		
3421.2	5	3421.3	2		
3418.7	5	3418.7	2		
3416.8	3	3417.1	2		
3414.3	2				
3412.4	2				
		3406.9	½		
3401.2	2				
3399.8	2				
3398.4	5	3398.3	1i.d.		
		3395.9	5i.d.		
3394.8	8				
		3393.9	4i.d.		
3392.5	6	3392.0	4i.d.		
		3389.3	4		
3386.7	7	3387.0	5		
3380	beginning of wide band	3384.7	4		
		3378.0	8		

TABLE I—*Continued*

λ for 3 Atmos. Pressure	Intensity and Character	λ for 2 Atmos. Pressure	Intensity and Character	λ for 1 Atmos. Pressure	Intensity and Character
		3375.9	9		
		3372.0	9	3372.1	2s.
		3365.9	9	3364.1	4s.
		3358.4	9	3358.7	8s.
		3351	beginning of wide band	3350.8	4s.
				3338.4	7
				3333.4	10
				3330	beginning of wide band

TABLE II

ABSORPTION SPECTRUM OF SULPHUR DIOXIDE AT LOW PRESSURES.

Length of Column of Gas = 207 cm				Length of Column of Gas = 20 cm	
λ for 1½cm. pressure	Intensity and Character	λ for 0.13 cm. Pressure	Intensity and Character	λ for 1.35 cm. Pressure	Intensity and Character
3226.2	2				
3211.4	1				
3207.6	1				
3203.4	1				
3198.3	3				
3195.4	4				
3190.3	1				
3187.1	1			3178.6	f.
3180.6	9	3180.7	2		
3171.5	8 n.h.				
3166.2	8 n.h.				
3157.5	10 h.				
3152.7	10 h.	3151.9	2		
		3149.8	½s.	3150.0	½
		3147.8	½s.		
3146.6	10 h.	3145.3	½		
		3143.1	½s.		
		3137.7	½		
3134	beginning of wide band	3131.0	5n.		
		3128.7	2s.	3129.3	1
		3125.7	2s.	3124.6	1
		3120.3	4n.		
		3111.3	5s.		
		3105.8	7	3104.7	6
		3101.4	4s.		
				3093.2	1s.
				3089.7	1s.
		3086.0	10	3086.2	8s.
				3084.2	2s.
				3082.4	2s.

TABLE II.—*Continued*

LENGTH OF COLUMN OF GAS = 207 CM				LENGTH OF COLUMN OF GAS = 20 CM	
λ for 1½ cm Pressure	Intensity and Character	λ for 0.13 cm Pressure	Intensity and Character	λ for 1.35 cm Pressure	Intensity and Character
		3064.9	10	3063.4	9
		3043.9	10	3042.6	9
		3022.6	10	3021.7	10
		3003.6	10 i.d.	3001.4	10
		2988	10 i.d.		
				2981.5	10
		2978	10 i.d.		
		2968	beginning of wide band	2962.0	10
				2943.0	10
				2927.	beginning of wide band
		2715.3	end of wide band		
		2701.5	9	2700.3	end of wide band
		2693.5	7	2692.3	9 i.d.
		2684.8	9	2683.7	10
		2676.7	7	2676.3	10
		2669.5	9	2668.6	10
		2660.1	8	2659.4	10
		2654.9	7	2653.2	9
		2653.3	7		
		2647 1	8	2646.6	9
		2643.0	7	2642.9	8
		2638.0	8	2637.3	9
		2633.0	7n.	2632.7	8
		2627.5	5	2627.1	7
		2623.1	5		
		2620.9	5	2621.2	8
		2616.9	5		
		2615.4	5		
		2613.7	7s.	2613.8	7
		2611.4	4		
		2596.8	5	2596.2	5
		2591.4	4	2590.8	3
		2585.2	3		
				2583.5	4
		2582.7	3		
		2512.2	3		
		2495.9	4	2496.2	2
		2478.1	3	2477.6	1
		2471.6	3	2471.4	1
2467	end of wide band				
		2464.3	2		
2456.	9 i.d.	2454.1	7	2454.5	2
		2448.3	6	2447.9	1

TABLE II.—*Continued*

Length of Column of Gas = 207 cm				Length of Column of Gas = 20 cm	
λ for $1\frac{1}{2}$ cm Pressure	Intensity and Character	λ for 0.13 cm Pressure	Intensity and Character	λ for 1.35 cm Pressure	Intensity and Character
2439	9 v.i.d.				
		2433.1	3		
2415.5	9 i.d.				
2401	9 i.d.	2401.0	2		
2397	8 i.d.	2397.5	1		
2379	8 i.d.				
2372	8 i.d.				
2367	8 i.d.				
2349	8 i.d.				
2345.5	8 i.d.				
2339	6 i.d.				
2327.5	7 i.d.				
2324	7 i.d.				
		2318.4	5		
		2308.7	6n.		
2304	6 i.d.	2303.2	8		
2297	7 i.d.	2298.0	9	2298.4	6
		2290.5	4		
2290	beginning of second wide band				
		2277.5	10	2278.4	9n.
		2269.2	6		
				2258.6	10n.
		2250.4	beginning of second wide band	2251.0	beginning of second wide band

IV. DISCUSSION

The following changes in the absorption spectrum with reduction of pressure may be noticed; they are evident from the plates.

1. As the pressure is reduced from three atmospheres to two, and from two to one, the bands become narrower and fainter, and the less refracted end of the very wide continuous band retreats toward the shorter wave-lengths, this part of the continuous absorption being replaced by narrow bands.

2. At the low pressures—namely $1\frac{1}{2}$, 0.45, 0.13 cm—the above changes are more marked; the narrow bands existing at one or more atmosphere's pressure have entirely disappeared; the wide continuous band has retreated not only from the longer wave-lengths but also from the shorter; and there is very little absorption beween

λ 257 and 230 $\mu\mu$. At the lowest pressure used, a pressure somewhat less than 0.13 cm, the wide continuous band is entirely broken up into narrow bands.

The shortest wave-length photographed was 210 $\mu\mu$; from this wave-length to 230 $\mu\mu$ the absorption decreases with the pressure, but is ill-defined, probably on account of the weakness of the continuous background.

A set of photographs has been taken of the absorption by a column of gas 20 cm in length with the gas at a pressure of 1.35 cm. Since the product

$$(\text{pressure of gas})\times(\text{length of column of gas})=207\times0.13=20\times1.35\ ,$$

the number of molecules which the beam meets in traversing a column of gas 207 cm long at a pressure of 0.13 cm is the same as it meets in traversing a column 20 cm long at a pressure of 1.35 cm. Since the numbers of molecules met in the two cases is the same we might expect the absorption to be the same, provided the physical condition of the molecules is the same. It was found that the absorption spectrum obtained from the column of gas 20 cm long at a pressure of 1.35 cm, corresponds very closely with that obtained from the column of gas 207 cm long at a pressure of 0.03 cm, but certain bands in the former are shifted toward the more refracted end of the spectrum; this is obvious from the photograph.

Photographs with this short column at pressures of 1.0 and 0.53 cm show the wide continuous band being gradually broken up into narrow bands. It is intended to extend this part of the work at the earliest opportunity.

Any mathematical relation between the wave-lengths of the bands or their reciprocals is obscure, particularly at the pressures of one or more atmospheres. The reciprocals of the wave-lengths with their differences are shown in Table III.

The differences of the frequencies suggest that the bands are arranged in groups with roughly equal differences between the first bands of successive groups; or we may regard the bands as arranged in series with roughly equal differences between the reciprocals of successive members of a series. Where the members of a series are scattered in Table III, they have been collected at the foot of

TABLE III

Wave-Lengths and Their Reciprocals at Pressure of 2 Atmospheres

λ	$\frac{1}{\lambda}\times 10^7$	Successive Diff'r'nces	Group Differ.	λ	$\frac{1}{\lambda}\times 10^7$	Successive Diff'r'nces	Group Diff'r'nces
3881.5	2576.3			3486.2	2868.5		
		1.9				9.4	
3878.7	2578.2		35.7	3474.7	2877.9		
		33.8				26.4	26.4
3828.5	2612.0			3443.2	2904.3		
		36.0	36.0			6.8	
3776.4	2648.0			3435.1	2911.1		
		17.8				2.5	
3751.2	2665.8		20.7	3432.2	2913.6		
		2.9				8.6	
3747.2	2668.7			3422.1	2922.2		22.2
		32.9	32.9			0.7	
3701.5	2701.6			3421.3	2922.9		
		32.5	32.5			2.2	
3657.5	2734.1			3418.7	2925.1		
		2.3				1.4	
3654.4	2736.4			3417.1	2926.5		
		2.9				8.7	
3650.6	2739.3			3406.9	2935.2		
		11.4	25.7			8.4	
3635.4	2750.7			3398.3	2943.6		
		5.3				1.1	
3628.4	2756.0			3395.9	2944.7		
		3.8				1.8	26.0
3623.5	2759.8			3393.9	2946.5		
		22.6				1.7	
3594.0	2782.4		34.2	3392.0	2948.2		
		11.6				2.3	
3579.1	2794.0			3389.3	2950.5		
		36.9	36.9			2.0	
3532.4	2830.9			3387.0	2952.5		
		2.4				2.0	
3529.5	2833.3			3384.7	2954.5		
		5.8				5.8	
3522.2	2839.1			3378.0	2960.3		
		8.0				1.9	
3512.3	2847.1		23.4	3375.9	2962.2		25.1
		1.8				3.4	
3510.1	2848.9			3372.0	2965.6		
		2.4				5.4	
3507.2	2851.3			3365.9	2971.0		
		3.0				6.6	
3503.5	2854.3			3358.4	2977.6		
		7.7					
3494.0	2862.0						
		3.2	23.6				
3490.2	2865.2						
		3.3 (9.4)					

SERIES OF BANDS

$\frac{1}{\lambda}\times10^7$	Difference	$\frac{1}{\lambda}\times10^7$	Difference	$\frac{1}{\lambda}\times10^7$	Difference
I		II		III	
				2830.9	
		2847.1			23.4
2851.3			21.4	2854.3	
	26.6	2868.5			
2877.9			45.1 $=22.5\times2$		68.6 $=22.9\times3$
	26.4				
2904.3					
	22.2	2913.6			
2926.5			21.6	2922.9	
	26.0	2935.2			23.6
2952.5			19.3	2946.5	
	25.1	2954.5			24.5
2977.6				2971.0	

AT PRESSURE OF 1½ CM

λ	$\frac{1}{\lambda}\times10^7$	Successive Diff'r'nces	Group Diff'r'nces	λ	$\frac{1}{\lambda}\times10^7$	Successive Diff'r'nces	Group Diff'r'nces
3226.2	3099.6			2456	4071.5		
		14.3				28.5	28.5
3211.4	3113.9		18.0	2439	4100		
		3.7				40	40
3207.6	3117.6			2415.5	4140		
		4.1				25	
3203.4	3121.7			2401	4165		32
		5.0				7	
3198.3	3126.7			2397	4172		
		2.8	20.0			31.5	31.5
3195.4	3129.5			2379	4203.5		
		5.0				12.5	
3190.3	3134.5			2372	4216		23.5
		3.1				11	
3187.1	3137.6			2367	4225		
		6.5				32	32
3180.6	3144.1			2349	4257		
		9.0	20.8			6.5	
3171.5	3153.1			2345.5	4263.5		18
		5.3				11.5	
3166.2	3158.4			2339	4275		
		8.7				21.5	
3157.5	3167.1			2327.5	4296.5		28
		4.8	19.6			6.5	
3152.7	3171.9			2324	4303		
		6.1				37	37
3146.6	3178.0			2304	4340		
						14	
				2297	4354		

SERIES OF BANDS

$\frac{1}{\lambda}\times 10^7$	Difference	$\frac{1}{\lambda}\times 10^7$	Difference	$\frac{1}{\lambda}\times 10^7$	Difference
I		II		III	
3099.6		3113.9		3117.6	
	22.1		20.6		20.0
3121.7		3134.5		3137.6	
	22.4		18.6		20.8
3144.1		3153.1		3158.4	
	23.0		18.8		19.6
3167.1		3171.9		3178.0	

AT PRESSURE OF 0.13 CM

λ	$\frac{1}{\lambda}\times 10^7$	Successive Differences	Group Differences
3180.7	3144.0		
		28.7	
3151.9	3172.7		
		2.1	
3149.8	3174.8		
		2.0	
3147.8	3176.8		
		2.5	
3145.3	3179.3		
		2.4	
3143.1	3181.7		
		5.3	
3137.7	3187.0		20.0
		6.9	
3131.0	3193.9		
		2.3	
3128.7	3196.2		
		3.1	
3125.7	3199.3		
		5.5	
3120.3	3204.8		20.5
		9.3	
3111.3	3214.1		
		5.7	
3105.8	3219.8		
		4.6	
3101.4	3224.4		20.6
		16.0	
3086.0	3240.4		
		22.3	22.3
3064.9	3262.7		
		22.6	22.6
3043.9	3285.3		
		23.1	23.1
3022.6	3308.4		
		20.9	20.9

λ	$\frac{1}{\lambda}\times 10^7$	Successive Differences	Group Differences
3003.6	3329.6		
		17.3	17.3
2988	3343.6		
2701.5	3701.6		
		11.0	
2693.5	3712.6		
		12.1	
2684.8	3724.7		23.3
		11.2	
2676.7	3735.9		
		11.1	
2669.5	3746.0		21.3
		13.2	
2660.1	3759.2		
		7.4	
2654.9	3766.6		
		2.3	
2653.3	3768.9		24.4
		8.8	
2647.1	3777.7		
		5.9	
2643.0	3783.6		
		7.2	
2638.0	3790.8		
		7.1	22.3
2633.0	3797.9		
		8.0	
2627.5	3805.9		

AT PRESSURE OF 0.13 CM (CONTINUED)

λ	$\frac{1}{\lambda}\times10^7$	Successive Differences	Group Differences
		6.4	
2623.1	3812.3		
		3.2	
2620.9	3815.5		
		5.8	20.1
2616.9	3821.3		
		2.2	
2615.4	3823.5		
		2.5	
2613.7	3826.0		
		3.4	
2611.4	3829.4		
		21.5	21.5
2596.8	3850.9		
		8.0	
2591.4	3858.9		
		9.3	21.0
2585.2	3868.2		
		3.7	
2582.7	3871.9		
2512.2	3980.6		
		26.0	26.0
2495.9	4006.6		
		28.8	28.8
2478.1	4035.4		
		10.6	
2471.6	4046.0		22.5
		11.9	

λ	$\frac{1}{\lambda}\times10^7$	Successive Differences	Group Differences
2464.3	4057.9		
		16.9	
2454.1	4074.8		26.6
		9.7	
2448.3	4084.5		
		25.5	25.5
2433.1	4110.0		
		54.9	2×27.5
2401.0	4164.9		
		6.1	
2397.5	4171.0		
2318.4	4313.3		
		18.1	
2308.7	4331.4		28.5
		10.4	
2303.2	4341.8		
		9.8	
2298.0	4351.6		
		25.3	25.3
2290.5	4376.9		
		13.9	
2277.5	4390.8		29.9
		16.0	
2269.2	4406.8		

SERIES OF BANDS

$\frac{1}{\lambda}\times10^7$	Difference	$\frac{1}{\lambda}\times10^7$	Difference	$\frac{1}{\lambda}\times10^7$	Difference
I		II		III	
3701.6					
	23.1	3712.6			
3724.7			23.3		
	21.3	3735.9			
3746.0			23.3		
	22.9	3759.2			
3768.9			24.4	3777.7	
	21.9	3783.6			20.2
3790.8			22.3	3797.9	
	21.5	3805.9			23.4
3812.3			20.1	3821.3	
		3826.0			
			24.9		
		3850.9			
			21.0		
		3871.9			

LENGTH OF COLUMN OF GAS = 20 CM
AT PRESSURE OF 1.35 CM

λ	$\frac{1}{\lambda}\times 10^7$	Successive Differences	Group Differences
3178.6	3146.4		
		28.2	28.2
3150.0	3174.6		
		21.0	21.0
3129.3	3195.6		
		4.8	
3124.6	3200.4		
		20.5	20.5
3104.7	3220.9		
		12.0	
3093.2	3232.9		
		3.7	
3089.7	3236.6		21.4
		3.6	
3086.2	3240.2		
		2.1	
3084.2	3242.3		
		1.9	
3082.4	3244.2		22.0
		20.1	
3063.4	3264.3		
		22.4	22.4
3042.6	3286.7		
		22.7	22.7
3021.7	3309.4		
		22.4	22.4
3001.4	3331.8		
		22.2	22.2
2981.5	3354.0		
		22.1	22.1
2962.0	3376.1		
		21.8	21.8
2943.0	3397.9		

λ	$\frac{1}{\lambda}\times 10^7$	Successive Differences	Group Differences
2692.3	3714.3		
		11.9	
2683.7	3726.2		22.2
		10.3	
2676.3	3736.5		
		10.8	
2668.6	3747.3		23.7
		12.9	
2659.4	3760.2		
		8.8	
2653.2	3769.0		
		9.4	23.5
2646.6	3778.4		
		5.3	
2642.9	3783.7		
		8.1	
2637.3	3791.8		
		6.6	22.8
2632.7	3798.4		
		8.1	
2627.1	3806.5		
		8.5	
2621.2	3815.0		19.3
		10.8	
2613.8	3825.8		
		26.0	26.0
2596.2	3851.8		
		8.0	
2590.8	3859.8		18.9
		10.9	
2583.5	3870.7		
2496.2	4006.1		
		30.1	
2477.6	4036.2		
		10.1	
2471.4	4046.3		
		27.9	
2454.5	4074.2		
		10.9	
2447.9	4085.1		
2298.4	4350.9		
		38.1	
2278.4	4389.0		
		38.5	
2258.6	4427.5		

SERIES OF BANDS

$\frac{1}{\lambda} \times 10^7$	Difference	$\frac{1}{\lambda} \times 10^7$	Difference	$\frac{1}{\lambda} \times 10^7$	Difference
3714.3					
	22.2	3726.2			
3736.5			21.1		
	23.7	3747.3			
3760.2			21.7		
	23.5	3769.0			
3783.7			22.8	3778.4	
	22.8	3791.8			20.0
3806.5			23.2	3798.4	
		3815.0			27.4
				3825.8	
					26.0
				3851.8	

the subdivisions of that table. These differences change gradually with the wave-length; they decrease from the longer to the shorter wave-lengths until the wide band is reached, then increase on the other side of it. The direction of this change corresponds with the change in absorption as the pressure is reduced; the bands decrease in intensity and eventually disappear first in the longer wave-lengths on the less refracted side of the wide band, and at the same time in the shorter wave-lengths on the more refracted side.

Region	Mean Difference in Frequency
380 to 350 $\mu\mu$	34
350 to 330 $\mu\mu$	25
330 to 313 $\mu\mu$	20
318 to 298 $\mu\mu$	21
272 to 258 $\mu\mu$	22
250 to 230 $\mu\mu$	30

Photographs taken with the column of gas 20 cm long show a rather more regular structure of bands; also some groups or series.

These groups of bands or series, combined with the breaking up of the wide continuous band into a considerable number of narrow bands as the pressure is reduced, suggest the possibility that all these bands may eventually be found to consist of very narrow bands or lines.

V. CONCLUSION

Although the series are at least in some cases incomplete and the differences in the wave-numbers are not equal, yet the near approach of these differences to equality with one another cannot be ignored. Thus this spectrum appears to consist of series of bands which follow approximately a law of equal differences. With the gas under conditions of pressure and temperature other than those tried, it may be found that its spectrum consists of quite definite series which follow closely a law of equal differences between the wave-numbers.

II. THE BAND EMISSION SPECTRUM OF SULPHUR DIOXIDE

I. APPARATUS AND METHOD

The usual conditions necessary to maintain the gas as a compound while under the electrical discharge were obtained as follows: The feeble electrical excitation was obtained from the secondary of a ten-inch induction coil, the primary of which was supplied with the current from three storage cells; the terminals of the secondary were placed too far apart for a spark to pass between them, and the vibrator was adjusted loosely. The spectrum tube had outside electrodes of lead foil with a layer of mica between them and the glass walls. As a further aid in preventing the decomposition of the gas, electrolytically prepared oxygen was mixed with the sulphur dioxide in the spectrum tube.

The sulphur dioxide was obtained from liquid sulphur dioxide which had been redistilled. The gas was dried by passing it through a bulb closely packed with phosphorus pentoxide; it was then admitted to the apparatus through a barometer column. Interposed between the barometer column and the spectrum tube were two U-tubes, one containing gold foil to absorb mercury vapor, and the other packed with phosphorus pentoxide to insure more perfect dryness of the gas. Similar tubes were interposed between the other end of the spectrum tube and the McLeod gauge and vacuum pump. All connections of the apparatus from the barometer column to the far side of the pump were either blown glass joints or mercury seal joints.

The spectrum tube was cleaned by soaking it in chromic acid

for ten or twelve hours, then washing it with distilled water, then with nitric acid, and again with distilled water; it was then dried by keeping it at a temperature of from 110° to 120° C. for eight or ten hours, meanwhile drawing a current of dry air through it. No bands from carbon compounds nor any of the strong hydrogen lines were ever seen or found on a photographic plate. The tube was exhausted, sparked, filled with oxygen, re-exhausted, and the process repeated until no air lines appeared.

The oxygen was prepared electrolytically from a 20 per cent. solution of crystallized phosphoric acid and dried by passing it through two bulbs loosely packed with phosphorus pentoxide and then through a U-tube closely packed with the same and plugs of glass wool. The line spectrum of oxygen was photographed in the region between λ 327 and 432 $\mu\mu$. It is well known that oxygen has no bands in this region.

As a standard spectrum that of the iron spark was used with the wave-lengths published by Kayser in his *Handbuch der Spectroscopie*, Vol. I.

The spectral apparatus was a Rowland concave grating mounted on the Rowland plan; it has a radius of 180 cm (5 ft. 11 in.), 15,028 lines to the inch, and a ruled surface 52 mm ($2\frac{7}{8}$ in.) wide. The wave-lengths were determined in the usual way by measurements made by means of the dividing engine mentioned above; the reduction factor was approximately 9.3 tenth-meters to 1 mm.

II. RESULTS

The chief difficulty in obtaining the spectrum of the compound lay in the extreme faintness of the light and the long exposures necessary. With the light from the capillary used "end-on" and a slit-width of about 0.05 mm, a continuous exposure of 45 hours gave only weak bands in the ultra-violet and very weak bands in the violet; the lines of the bands were too coarse for measurement. The wave-lengths of the heads of the bands obtained from this photograph are given in Table IV. A continuous exposure of 69 hours with a slit-width of 0.035 mm approximately gave bands too faint for measurement. A continuous exposure of 91 hours with a slit-width of 0.018 mm approximately was spoiled by ham-

mering in another room in the building. For the spectrum for which measurements are given the pressure of sulphur dioxide was 0.27 cm, and the pressure of oxygen 0.28 cm making a total pressure of 0.55 cm at the beginning of the exposure. During exposure, oxygen and sulphur dioxide were added to try to keep the condition of the tube constant; the total pressure at the end of the exposure was 0.45 cm. Hitherto no attempt has been made

TABLE IV

BAND EMISSION SPECTRUM OF SULPHUR DIOXIDE

WAVE-LENGTHS OF THE HEADS OF THE BANDS AND THEIR RECIPROCALS

	λ	Intensity and Character	$\frac{1}{\lambda}\times 10^7$	Successive Differences
1	3271.4	4	3056.8	
2	3383.7	5	2955.3	101.5
3	3428.0	4	2917.1	38.2
4	3502.2	5	2855.2	61.9
5	3548.7	5	2817.9	37.3
6	3628.0	4	2756.3	61.6
7	3675.9	5	2720.4	35.9
8	3726.5	2	2683.5	36.9
9	3761.5	f	2658.5	25.0
10	3811.3	5	2623.8	34.7
11	3862.7	2	2588.8	35.0
12	3954.6	5 h.	2528.7	60.1
13	4007.6	4 h.	2495.2	33.5
14	4040.6	3 v.i d.	2474.9	20.3
15	4107.3	2 i.d.	2434.7	40.2
16	4145.5	2	2412.3	22.4
17	4153.4	2	2407.7	4.6
18	4163.0	3 h.	2402.1	5.6

TABLE V

SERIES OF BANDS

$\frac{1}{\lambda}\times 10^7$	Difference	$\frac{1}{\lambda}\times 10^7$	Difference	$\frac{1}{\lambda}\times 10^7$	Difference
I		II		III	
1) 3056.8		3) 2917.1		8) 2683.5	
	101.5		99.2		94.7
2) 2955.3		5) 2817.9		11) 2588.8	
	100.1		97.5		93.6
4) 2855.2		7) 2720.4		13) 2495.2	
	98.9		96.6		93.1
6) 2756.3		10) 2623.8		18) 2402.1	
	97.8		95.1		
9) 2658.5		12) 2528.7			
			94.0		
		15) 2434.7			

to photograph this spectrum in regions of greater wave-length where longer exposures would be necessary.

The spectrum thus obtained consists of bands with distinct heads turned toward the ultra-violet, and is thus characteristically different from the "band" or compound line spectrum of elementary sulphur obtained by Eder and Valenta, and published in their paper, "Die Spectren des Schwefels," 1898.

The reciprocals of the wave-lengths (Table IV) show that the bands can be arranged in three series with decreasing difference of wave-numbers (Table V). The series will be seen to follow roughly Deslandres' law. These series are doubtless incomplete, as the range photographed covers only 105 $\mu\mu$.

My investigation of the spectrum of sulphur dioxide was begun originally at the suggestion of Professor A. Stanley Mackenzie with the purpose of comparing it with that of sulphur as determined by Runge and Paschen and by Eder and Valenta. Owing to various causes, this plan was not carried into effect, and the research as described in the preceding pages was proposed by Professor J. S. Ames, to whom I desire to express my indebtedness and my gratitude for his kindness in directing my work and for his invaluable suggestions in the carrying out of this investigation. I wish at the same time to express my thanks to Dr. H. W. Springsteen, ass-

ciate in physics, for the generosity with which he has provided me with the laboratory apparatus needed for this piece of work; also to Dr. W. B. Huff, professor of physics, and to Dr. E. P. Kohler, professor of chemistry, for frequent help and encouragement, particularly during the early part of my work.

BRYN MAWR COLLEGE,
March 31, 1906.

LIFE

Fanny Lowater attended the University College, Nottingham, England, as an undergraduate student during 1889–1891 and 1892–1893, taking courses of lectures preparatory to the degree of Bachelor of Science of the University of London. The subjects studied were Pure and Applied Mathematics, Physics, Chemistry, and Biology. She spent the year 1891–1892 at Newnham College, Cambridge, where she attended lectures in Physics by Professor J. J. Thomson and read Mathematics with the Newnham instructors.

In 1894 she came to Bryn Mawr College as Assistant Demonstrator in Physics and held that position during the years 1894–1896 and 1897–1898, and in the meantime attended graduate lectures in Physics by Professor A. Stanley Mackenzie and Dr. Edgar Buckingham. During the year 1898–1899 she was Acting Secretary of the College, and from 1899 to 1905 Demonstrator in Physics.

She held the Fellowship in Physics for the year 1896–1897, when Professor Mackenzie suggested that she should investigate the spectrum of elementary sulphur; but after Runge and Paschen had published the *Compound Line Spectrum of Sulphur* in 1897, Professor Mackenzie suggested that she should investigate the spectrum of sulphur dioxide and compare it with the spectrum of sulphur found by Runge and Paschen; in the following year Eder and Valenta published *Die Spectren des Schwefels.*

During the present year, at the suggestion of Professor J. S. Ames, of Johns Hopkins University, she has made an investigation of the absorption spectrum of sulphur dioxide and an incomplete investigation of the band spectrum of the same gas; she presents this work as a dissertation for the degree of Doctor of Philosophy of Bryn Mawr College. During the years 1902–1905 she attended lectures in Pure and Applied Mathematics by Professor C. A. Scott, Mr. J. Harkness, and Mr. J. E. Wright; she offers these as subordinate subjects and Physics as the principal subject for the same degree.